



Research Paper

ATMOSPHERIC PLASMA SPRAY COATINGS OF AL₂O₃-YSZ SYSTEM FOR HIGH TEMPERATURE APPLICATIONS

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Thermal barrier coatings (TBCs) used in gas-turbine engines afford higher operating temperatures, resulting in enhanced efficiencies and performance. Here we demonstrate the use of the commercial manufacturing method of atmospheric-plasma-spray (APS) to fabricate Yttria-stabilized zirconia (YSZ)-based TBCs. Thermal Barrier Coatings (TBCs) of Al₂O₃ - 7-8% YSZ were deposited by Atmospheric Plasma Spray (APS) method onto stationary flat Nickel super alloy substrate. This paper describes the APS technique for creating a bond coat of Al₂O₃ and a top coat of 7-8% YSZ to resist the thermal shock and for high temperature applications. Phase characterization was done by X-ray diffraction and micro structural characterization by scanning electron microscopy. The porosity and mechanical characterizations were also determined by SPIP software. The observations suggest that the surface morphology plays a significant role in determining the thermal resistance of the coated surface. These coatings and many other such coating techniques provides with resistance of heat fluxes and retain the original strength of the material even after subjecting it to high thermal shock.

Keywords: Atmospheric plasma spray, SPIP, Zirconia coating, Microstructure characterization

INTRODUCTION

The materials with superior performance both in mechanical strength and oxidation resistance are required to be applied for high temperature applications. Thermal-barrier systems are an excellent example of multi-layered, multifunctional material assemblies that have enabled substantial improvements in the performance and efficiency of gas

turbine engines. The combination of a metallic substrate, an inter metallic (or mixed metallic and inter metallic) interlayer, and a low conductivity ceramic top coat permits the system to operate near, or even above, the melting point of the substrate in a highly oxidizing combustion environment. Inter metallic coatings have long been a central requirement for high temperature operation

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of propulsion and power generation systems. In early applications in aero and land based turbines (before ceramic thermal barriers were developed), environmental coatings typically served a single function. Aluminide-type coatings based on NiAl and NiCoCrAl-family coatings became the standard systems for oxidation protection, while diffusion chromides and overlay CoNiCrAl materials were used to protect against hot corrosion. As turbine operating temperatures have increased, fuels have become cleaner, substrate alloys have evolved to refractory rich nickel-based single crystals, and environmental coatings have become multifunctional. Thermal barrier coating systems on super alloys combine a thermal insulating zirconia top coat, which has a relatively low thermal conductivity and large thermal expansion coefficient compared with other technological ceramic, with a metallic bond coat that protects the substrate from both oxidation (usually with the development of stabilized protective thin layer) and hot corrosion when operated at high temperature. For ease and economy of fabrication, a graded thermal barrier coatings is comprised of finite number of layers, each have a certain ceramic-bond coat alloy proportions. Zirconia is an excellent refractory owing to its high melting point (about 2680°C), its low coefficient of expansion and thermal conductivity, and its resistance to chemical action so it is used as a raw material for TBC system. Pure ZrO_2 has three polymorphs. Monoclinic zirconia (m- ZrO_2) is stable up to 1170°C, where it transforms to tetragonal zirconia (t. ZrO_2), the later tetragonal zirconia changed into cubic zirconia (c- ZrO_2) at 2370°C and finally zirconia melt at 2680°C

(E Ryshkowitch and D W Richardson, 1985). The challenges are increasing for developing inter-metallic bond coatings that will reliably perform in present and future thermal engineering systems. New experimental and characterization tools and computational design approaches are to be explored and this paper makes an attempt towards future prospects for discovery of new materials and material combinations for prediction of their performance in complex thermo- mechanical environments.

EXPERIMENTAL PROCEDURE

The studies presented in the paper focus on gaining a systematic understanding of the influence of layered coatings on microstructure development in plasma-sprayed coatings. To do this, a fully quantitative microstructure characterization was carried out for aps sprayed coatings by SEM for each deposited layers. SPIP software gives the detailed theoretical results of the mechanical parameters of the coatings.

A. Fundamentals of Plasma Spray

Spray torch and in most cases (99%) plasma spraying is achieved by using plasma torches. A high intensity arc is operated between a stick type cathode and nozzle shaped water cooled anode. Plasma gas, introduced along the cathode, is heated by arc to plasma temperatures, leaving the anode nozzle as a plasma jet or plasma flame. Fine powder suspended in a carrier gas is injected into the plasma jet where the powder particles are accelerated and heated. As the molten powder particles impinge with high velocities on substrate, they form a more or less dense coating.

B. Plasma Generation and Formation

The arc is initiated between the tip of the cathode (typically thoriated tungsten) and the water cooled anode nozzle. The working gas is introduced either axially or with an additional swirl component. The latter improves arc stability in the vicinity of the cathode and rotates the anode arc root which is desirable for reducing anode erosion. The gas heated by the arc emanates as a plasma jet from the torch orifice. The gas flow rate is sufficiently high to ensure a highly turbulent jet with a visible length of several centimeters. Argon and mixtures of argon with other noble (He) or molecular gases (H₂, N₂, O₂ etc.) are frequently used for plasma spraying. The addition of He and in particular of molecular gases results in a drastic increase in the enthalpy of the plasma. The maximum temperature in the plasma jet is a function of the design and of the operating parameters.

C. Materials

In the present study C - 263 Nickel superalloy was used as substrate. All the specimens were in the shape of a flat plate (×40 mm). The specimen's surfaces were shot blasted with alumina grit in the range of 50-80 mesh and under a pressure of 40-50psi. The surface oxides were removed using methyl ethyl kethon cleaner, and degreasing was performed by trichloro ethylene vapor. After washing they were preheated at 150-200°F and finally coatings were applied over specimens. Argon was used as primary plasma gas whilst hydrogen was the secondary gas. Amdry 962 trade mark NiCrAlY micro-powders, micro-sized Metco 204NS-G trade mark YSZ conventional zirconia powders were used. The nano size

Yttria stabilized zirconia powders were prepared via chemical co-precipitation process, with particle sizes of <200nm, from plasma spray able agglomerated spherical micrometer sized granules (typical size range in 15-150µm) and coating was applied through plasma spraying. The plasma spraying was carried out with Metco 3MB atmospheric plasma spraying equipment. The NiCrAlY bond coat with a thickness of 150µm was plasma sprayed on the specimens. Having applied NiCrAlY coating, the specimens were then plasma sprayed with as follows: (a) Conventional YSZ coating with a thickness of 350µm, (b) Nano-structured YSZ coating with a thickness of 350µm. The main compounds in hot corrosion process were V₂O₅ and Na₂SO₄ which were prepared from high purity materials mixed in weight ratio of 55wt.% V₂O₅ and 45wt.% Na₂SO₄. 30mg of the mixture per square centimeter of specimen's surface was spread to form an even film of corrosive material on coating surface keeping 3 mm distance from the edge. The specimens were then placed in electric furnace in cyclic hot corrosion process at 1050°C in 4 hours duration. They were then inspected and their peripheral conditions were observed. If there were any cracks or spallation in coating edge the test stopped and the time was noted. It is to be mentioned that the test temperature and the concentration of corrosive materials were selected according to zirconia phase transformation temperature to accelerate the test. Also the mechanical properties of the coating were evaluated before and after hot corrosion tests. Optical microscopy (OM), scanning electronic microscopy (SEM, Oxford CAMSCANMV2300) equipped with energy

dispersive spectrometer (EDS) and X-ray diffraction (XRD, Philips X'pert) were used to study the specimens. Nano indentation tests were performed on the cross section of sample including; substrate, band coat and YSZ coating before and after hot corrosion. In this experiment, the mechanical properties comprising the hardness (H) and elastic modulus (E) were determined by using a nano indenter (Micro Materials LTD, wrexham, UK) with Berkovich tip. The average values for ten points were considered as H and E. The parameters which were used in nano indentation test are: maximum load = 100mN, loading rate = 5mN/S, unloading rate = 5mN/S and dwell period at maximum load = 10S.

suited for characterization and identification of polycrystalline phases.

Table 1: Process Parameters Employed for APS Coating of YSZ Top Coat	
Gas Flow	4.2m ³ /hr
Flame or Exit Plasma Temp.	5500°C
Particle impact velocity	240 m/s
Spray rate	5kg/hr
Power	30-80kw
SOD	50-60mm

RESULTS AND DISCUSSION

A. XRD

About 95% of all solid materials can be described as crystalline. When X-rays interact with a crystalline Substance diffraction pattern is obtained. Every crystalline substance gives a pattern the same substance always gives the same pattern and in a mixture of substances each produces its pattern independently of the others. The X-ray diffraction pattern of a pure substance is, therefore, like a fingerprint of the substance. The powder diffraction method is thus ideally

Figure 1: XRD Pattern for C-263 Substrate

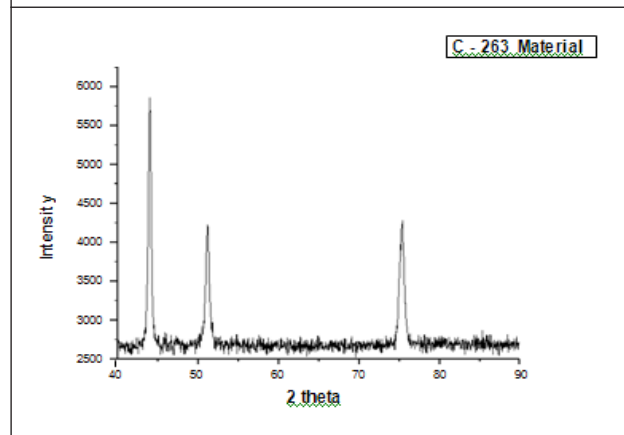


Figure 2: SEM Image Showing Surface of Bare Substrate

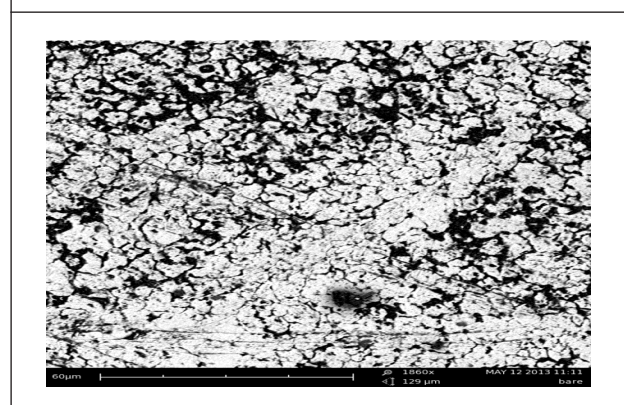


Figure 3: XRD Pattern for APS Deposit of Al₂O₃

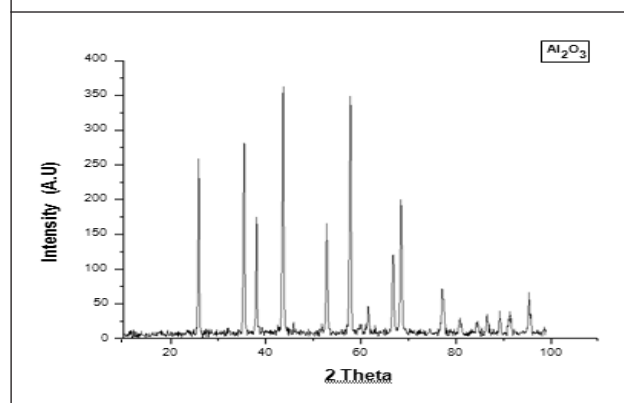


Figure 4: SEM Image Showing Surface After Al₂O₃ Bond Coat

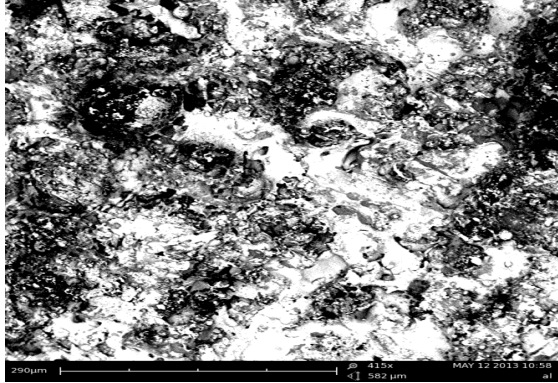
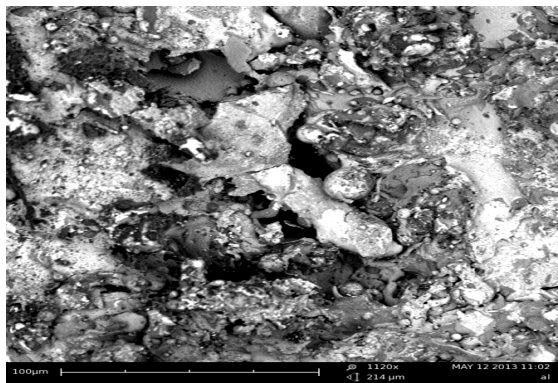


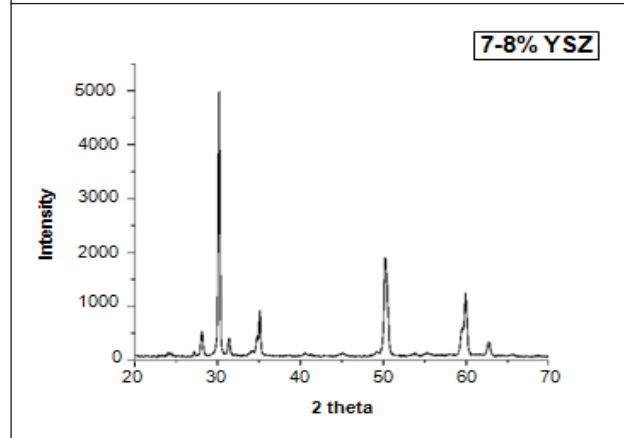
Figure 5: SEM Image Showing Point Defect in Al₂O₃ Bond Coat



XRD results demonstrated the formation of solid solution of Al and Al₂O₃ phases which could enhance the life time of the material. The more broadened diffraction peaks confirmed the formation of nano-crystallite since broadening was inversely proportional to crystallite size. However, broadening was associated with vacancies, point defects, lattice distortions and micro-strain developed during deposition process. Moreover, the concentrations of oxygen species associated with these parameters were directly coupled with the micro hardness which increased the

life time of the material. XRD data was also employed to estimate the residual stresses developed in Al₂O₃ layer. The up and down shifting of diffraction peaks from their stress free values indicated the existence of residual stresses. The peak shifting from their stress free values was due to diffusion of oxides interstitially which distorted the lattice, creating point defects and vacancies. The peak shifting could also be due to the removal of hydrogen creating vacancies resulted in the development of defects. It is well known that more diffusion could take place at high temperature which may shift the diffraction peaks from their corresponding stress free values (Figure 6).

Figure 6: XRD Pattern for Typical APS Deposit of YSZ



The young's modulus of Al₂O₃ layer ranged from 176 to 370 GPa depending on the deposition temperature and the purity of Al₂O₃ phase. The young's modulus of Al₂O₃ phase (500°C temperature) was found to be 344 GPa. In our case, the deposition temperature was 550°C which was very close to the above mentioned temperature for which the young's modulus of Al₂O₃ phase was 344 GPa. Thus, we multiplied the strain

with 344 GPa (young's modulus) in order to estimate the residual stresses developed in Al_2O_3 phase at 500°C temperature. The stress was found to be ~ - 0.53 GPa in Al_2O_3 layer deposited for 5 h treatment time where the negative sign indicated the compressive nature of stress.

Figure 7: SEM Image Showing Surface After APS Deposit of YSZ

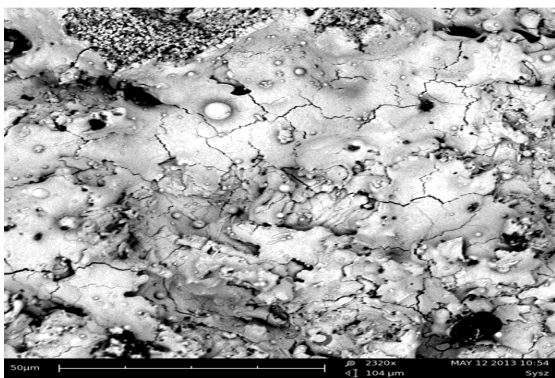
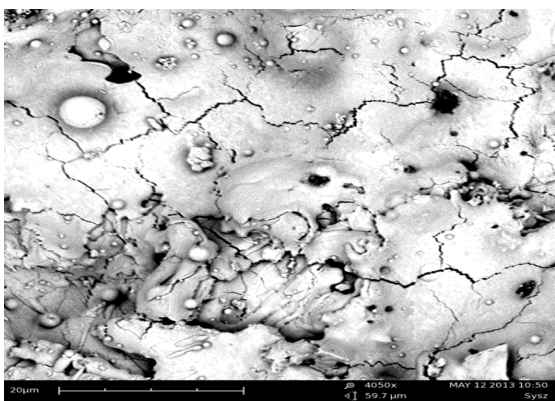


Figure 8: SEM Image Showing Spallation in YSZ Coating



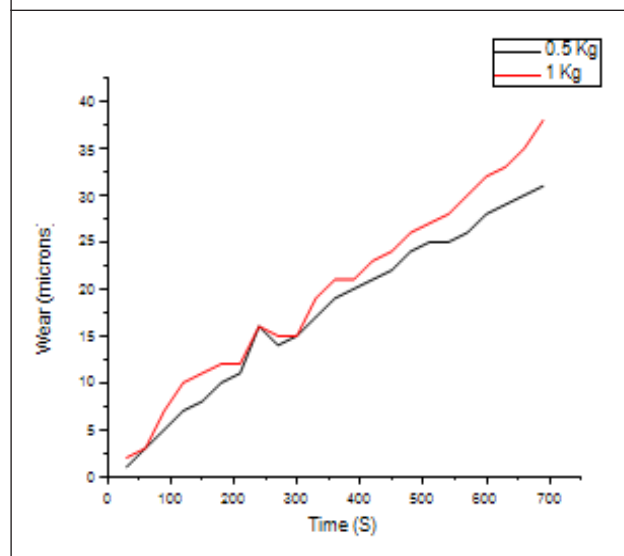
In X-ray diffraction technique, the position of the peaks indicates the crystal structure of the material while the intensity of the peaks depends on the material distribution in the structure (J R Connolly, 2010). All the heat-

treated YSZ+20Al+5Ti APS TBCs are found to contain one Al-lean t-ZrO₂ phase and α-Al₂O₃, in addition to minor amounts of TiO₂ and Y₂O₃ phases. The t-ZrO₂ phase in the 1200°C 24 h heat treated TBC shows higher tetragonality (1.015), which is the result of Al-depletion by diffusion and concomitant precipitation of α-Al₂O₃. Higher temperature heat-treatments (1300°C) result in even higher tetragonality in t-ZrO₂ phase, and are consistent with the higher concentrations of precipitated α-Al₂O₃. The heat-treatment of YSZ+20Al+5Ti APS TBC at 1300°C for 72 h results in about a third of the added Al₂O₃ remaining in solid solution in t-ZrO₂. XRD peak broadening analysis showed the same average α-Al₂O₃ precipitate size as the 1200°C (24 h) case: 200 nm.

B. Corrosion Rate

The weight losses of after the corrosion tests in a V₂O₅ and Na₂SO₄ corrosion environment at 1050°C as a function of the time are shown in figure 9.

Figure 9: Weight Loss of the Alloys Corroded at 650°C as a Function of Time



Under a high temperature oxidative molten salt environment, the reason for the weight loss of the specimens with time was attributed to a cracking of the protective layer which led to its spallation from the base metal surface. Therefore, it was concluded that the weight variations of a specimen would be greatly affected by the adhesive strength between a corrosion layer and a base metal by considering the formation, sustenance, and spallation of a corrosion layer and, also the stability of a corrosion layer's growth. The young's modulus of Al_2O_3 layer ranged from 176 to 370 GPa depending on the deposition temperature and the purity of Al_2O_3 phase. The young's modulus of Al_2O_3 phase (500°C temperature) was found to be 344 GPa. In our case, the deposition temperature was 550°C which was very close to the above mentioned temperature for which the young's modulus of Al_2O_3 phase was 344 GPa. Thus, we multiplied the strain with 344 GPa (young's modulus) in order to estimate the residual stresses developed in Al_2O_3 phase at 500°C temperature. The stress was found to be ~ -0.53 GPa in Al_2O_3 layer deposited for 5 h treatment time where the negative sign indicated the compressive nature of stress.

CONCLUSION

A number of new coating methods have been employed and older methods are being refined. Many analytical tools are introduced

which have gained importance for the fact of being much precise. The development and evaluation of the coatings have gained much priority and has become the basic need the development and evaluation of coatings are expensive and there is now a need, more than ever, to conserve resources, optimize test programmed and for a greater coordination dissemination of information. In this study, the TBC system was investigated using several processes to conclude the influence of plasma spray parameters on the coating performance, from the obtained data, discussion and interpretation of the results, it could be concluded that:

1. The total porosity of the APS coating decreases as the hydrogen flow rate increases. The SEM micrographs also reveal that uncontrolled hydrogen flow rate leads to cracking of the coatings. Achieving control of the microstructure of plasma-sprayed thermal barrier coating (TBC) systems offers an opportunity to tailor coating properties to demanding applications.
2. The presence of gaseous atmosphere during coating was mainly responsible for accelerating the powder particles. The higher particle velocity resulted in a worse melting behavior of the powder due to the shorter dwell time, leading to a lower coating thickness, namely a lower deposition efficiency of the powder.
3. As the injection angle decreases (or as the injection distance increases) led to increase the porosity, decrease the droplet temperature and decrease the number of droplets which impact normally.

4. It is worth noting that amorphous microcrystalline, and meta-stable phase are commonly observed in plasma sprayed materials due to the high rate (rapid solidification and rapid cooling) that are inherent in this process.
5. The deviation of the spray parameters from the optimum condition led to increase corrosion rates. Acknowledgment. This work is financially supported by Department of Science and Technology - Nano Mission, New Delhi.

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